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Thermal characteristics and fate of heavy metals during thermal treatment of *Sedum plumbizincicola*, a zinc and cadmium hyperaccumulator



Dao-Xu Zhong ^a, Zhao-Ping Zhong ^a, Long-Hua Wu ^b, Hui Xue ^a, Zu-Wei Song ^a, Yong-Ming Luo ^c

^a Key Laboratory of Energy Thermal Conversion and Control, Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, Jiangsu, China ^b Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, Jiangsu, China

^c Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, Shandong, China

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1. Introduction

Phytoextraction using hyper-accumulators is considered to be an efficient and low cost technology to remove heavy metals from contaminated soils [1]. *Sedum plumbizincicola (S. plumbizincicola)*, a zinc and cadmium hyperaccumulator, has considerable capability to extract Zn and Cd has been demonstrated to successfully remediate Zn and Cd contaminated soils [2,3].

It has been reported [3,4] that S. plumbizincicola can produce large biomass containing several thousands of mg Zn/kg and more than one hundred mg Cd/kg will be produced by plants widely grown at a phytoremediation site in Zhejiang Province, east China, Therefore, the safe and economical disposal of the harvested biomass to avoid secondary environmental pollution is a complex problem. When comparing general disposal methods for the contaminated biomass such as composting, compaction, incineration, ashing, pyrolysis, direct disposal, and liquid extraction, incineration is the preferred and recommended option [5]. Thermal disposal methods (incineration or gasification) are feasible and economically acceptable methods that present two advantages. Firstly they involve more than 90% reduction in the volume of the waste and secondly they destroy organic compounds (near complete). On the other hand, the metal species contained in the waste are not destroyed during high-temperature incineration, but instead condense to form metallic particles during the cooling of the flue gas. Therefore, thermal methods are applicable for metal recovery in cases where the metals are mainly concentrated in solid residues. Metal extraction and recovery from ashes have already been employed industrially for municipal waste incineration plants [6]. In addition, the behaviour and

ABSTRACT

A horizontal tube furnace was designed to test the disposal of ground hyperaccumulator biomass. X-ray diffraction (XRD), thermodynamic analysis and chemical extraction were used to characterise the heavy metals. The recoveries of Zn, Pb, and Cd in bottom ash decreased with increasing incineration temperature but increased in fly ash. The recoveries of Zn, Pb, and Cd fluctuated with increasing air flow rate and most of the metals were found in the fly ash. Cd, Pb, and Zn occurred during the combustion process in the form of elementary substances and their oxides. During reduction in the thermal process both Pb and Cd formed metal complexes such as $Ca_{0.75}Cd_{0.25}O$ and $Pb_2O_{3.333}$ or their mixtures and more of the bottom ash Zn under the reducing conditions was present as pure metal, crystalline oxides, sulphides or complex compounds combined with other metals.

transportation of heavy metals (HMs) during thermal disposal are complex functions of the incinerator operating conditions (including temperature and gas composition) [7–9], the composition of the hyperaccumulator, and the physico-chemical properties of the metals and their compounds (chlorine, sulphur, or alumino-silicates). This is the purpose of studying the behaviour of heavy metals at different temperatures and oxygen concentrations in the combustion gas. In addition, it is important to understand the ash fractions and how HMs will behave during thermal disposal processing.

Some studies related to phytoextraction biomass have been based on theoretical calculations or incinerator operating conditions. Liung and Nordin [10] modelled the fate of ash-forming elements and HMs during simulation of combustion of Salix species within the temperature range of 100 to 1600 °C but Lundholm et al. [11] reported some fundamental differences in input thermodynamic data from various databases leading to differences in equilibrium calculations from study to study. Wu et al. [17] investigated the control of HM emissions from incineration and found that kaolin and activated carbon removed most of the Cd from the flow gas. Yan et al. [12] investigated the volatilization behaviour of arsenic (As) and its mechanism during incineration of Pteris vittata. Lu et al. [13] reported that incineration favours the volatilization of Cd in contrast to pyrolysis and the contents of HMs in ashes and flow gas were studied in S. plumbizincicola. Lind et al. [14] combusted forest residues and found that heavy metal behaviour in reducing and oxidizing atmospheres was generally different.

In the case of hyper-accumulators, most of the incineration tests have focused on the transport of HMs during thermal treatment or reduced HM concentrations not exceeding the emission standards. The

126

Table 1

Proximate and ultimate analysis (wt.%) of S. plumbizincicola.

Proximate analysis			Ultimate analysis					Calorific value (kJ/g)
A	VM	М	С	Н	Ν	S	0	
8.17	76.33	15.5	40.2	6	1.1	0.1	45.3	15.188

Ultimate analysis data and proximate analysis data are expressed on dry (bd) basis. Calorific value is higher calorific value.

interactions between hyper-accumulator composition and the physicochemical properties of the metals and their compounds (chlorine, sulphur, or alumino-silicates) greatly affect the bottom ash metal distribution [15–17]. Further tests on the behaviour of heavy metals during *Sedum* plant incineration are therefore needed to reveal the transformation of toxic elements and then the mechanisms for methods on reducing their emissions.

The objectives of the present study were to experimentally quantify the impact of temperature, air excess ratio and compounds (chlorine, sulphur, or alumino-silicates) in S. plumbizincicola on the partitioning of heavy metals under simulated incineration conditions and to understand their speciation using thermodynamic calculations. The partitioning of HMs under different incineration conditions was predicted thermodynamically in a well-defined system whose composition corresponded to that during the incineration of hyper-accumulators. The equilibrium calculations focused on the influence of the operating temperature, air excess ratio and compounds (chlorine, sulphur, or alumino-silicates) in the combustion residues and flow gas on heavy metal speciation. The thermodynamic calculations focused on the influence of operating temperatures in the range of 350-1950 °C and the oxygen contents in the combustion gas. The theoretical thermodynamic results were then compared with several analytical results (XRD and sequential chemical extraction) related either to the HM distribution among bottom ash, fly ash and flue gas from different temperatures and air flow rates or to the chemical species in the samples from tubular furnace reactor experiments. The study focused on Zn, Cd, and Pb but the behaviour of other compounds found in S. plumbizincicola such as S, Al, Ca, Si, and Cl was also briefly studied.

2. Materials and methods

2.1. Materials

S. plumbizincicola biomass was collected from the location where it was originally found at a Pb/Zn mine area in Chun'an City, Zhejiang Province, east China. The biomass for combustion tests was dried at 85 °C in an oven for 8 h before testing in a horizontal quartz tube. The proximate and ultimate analysis of *S. plumbizincicola* is shown in



Fig. 2. Thermodynamic equilibrium calculations of incineration (M: elements of *S. plumbizincicola*).

Table 1. The elemental compositions (mg/kg) of *S. plumbizincicola* were 9838 \pm 289 (Zn), 560 \pm 6 (Cd), 62.5 \pm 3.7 (Pb), 77.6 \pm 1.7 (Cu), 45.4 \pm 6.0 (Cr), 642 \pm 46 (Fe), 84.8 \pm 6.9 (Na), 13976 \pm 543 (Al), 61886 \pm 805 (Ca), and 1135 \pm 15 (Cl), respectively; and the SiO₂ content was 850 mg/kg.

2.2. Experimental facility

The experimental facility, shown in Fig. 1, contained two high pressure gas sources (O₂, N₂), a flow control valve and meter, a horizontal guartz tube with a surrounding electrically heated furnace, and a flue gas absorption device. The horizontal quartz tube had an inner diameter of 45 mm and a length of 1000 mm, of which 400 mm was in the temperature controlled reaction zone heated and controlled by the electrical furnace from 100 to 1100 °C. All flue gas samples were collected in each experiment. The absorption device was based on US EPA Method 29. The joint between the quartz tube and the absorption bottle was plugged with glass fibre filter material to sample the fly ash. The experiments were performed at temperatures from 350 to 950 °C and air flow rates of 0.5, 0.75, 1.0, and 1.2 L/min. About 3 g of S. plumbizincicola powder was placed in a dried and weighed quartz weighing boat and transferred into the centre of the quartz tube which was pre-heated to the desired temperature. The gas flow was introduced into the quartz tube before the start of the experiments. After each experiment the absorption bottles containing 5% HNO₃ + 10% H₂O₂ solution were removed and replaced by another set of bottles to dispose of the exhaust gas. Bottom ash and fly ash were carefully taken out, allowed to cool to room temperature, weighed, and sealed in a sampling bag.

2.3. Determination of heavy metals

Solid samples of fly ash and bottom ash were digested with a solution of HNO_3 , $HClO_4$ and HF (3:2:1 HNO_3 : $HClO_4$:HF by volume) for



Fig. 1. Schematic diagram showing the setup of the horizontal tube furnace. NB: 1, high-pressure O₂; 2, high-pressure N₂; 3, flow meter; 4, horizontal quartz tube; 5, electrically heated furnace; 6, quartz boat; 7, temperature controller; 8, fibreglass filter 9, iced-water bath; 10, absorption solution 1 (5% HNO₃ + 10% H₂O₂); 11, silica gel.



Fig. 3. S. plumbizincicola incineration process flow sheet (B1: RGibbs block; B3: Ryield block; MT: stream for S. plumbizincicola; AIR: stream for air; 3: stream between B3 and B1; 2: output stream).

determination of Cd, Zn, and Pb. Then the Zn and Pb concentrations were determined by flame atomic absorption spectrophotometry (Varian SpectrAA 220FS). The solution Cd concentration was determined with a Varian SpectrAA 220Z spectrophotometer using a graphite furnace.

2.4. Equipment and method for TG-DTG experiment

A TG-DTG (SetaramSetsys evolution 16) analyser was used to study the evolution of weight and volatile matter of *S. plumbizincicola* biomass during pyrolysis and combustion. Approximately 20 mg of the sample was used for pyrolysis and 10 mg for combustion in this study. It was crushed to a powder finer than 0.2 mm. Room temperature to 800 °C was set as the temperature range and the heating rate was set at 10 °C/min. Nitrogen was used as the inert gas during pyrolysis and air was used during combustion.

2.5. Thermodynamic simulation by advanced system for process engineering (ASPEN)

Combustion of *S. plumbizincicola* constitutes a multi-component and multi-phase system. To identify the dominant species of each element the principle of minimising the total Gibbs free energy of the system was used to calculate the thermodynamic equilibrium. The final equilibrium state is obtained by determining all possible species that can be derived from the elements of the input system. The analysis serves to determine the major metallic species and to predict the possible chemical interactions between the HM and the matrix components (Fig. 2).

The process flow-sheet consists of two blocks (Ryield and Rgibbs) and four streams (Fig. 3). Material stream (MT stream) pyrolysis in the Ryield block and then incineration in the RGibbs block. The flow rate of the material stream was set at 20 kg/h and the air excess ratio set at 1.2.

2.6. Chemical extraction series

The operating conditions of each step are described in Table 2. Steps 3 and 4 determined the "easily reducible" and the "moderately reducible" phases, respectively, as defined by Kersten and Förstner [15]. A boric acid attack to dissolve possible fluoride precipitates and to eliminate the HF excess supplemented the last extraction step. To respect fixed pH procedures, HNO₃ was added during steps 1 and 2 to maintain

Table	2

Procedure of chemical extraction series.

the pH of the solution. The solid to extract ant ratio was 1 g 10 $\rm ml^{-1}$ for all steps.

3. Results and discussion

3.1. TG-DTG studies on S. plumbizincicola

As displayed in Fig. 4, the pyrolysis process of the sample can be divided into three steps. At the first step, moisture evaporated when the temperature was less than 170 °C, about 9.51% of the S. plumbizincicola biomass. The second step, the fast decomposition stage, was from 170 to 400 °C. Hemicelluloses and cellulose cracks in this state were lost, peaked at 306 °C, and about 50.8% of the weight of S. plumbizincicola was lost during this stage. At the third step further cracking of fixed carbon occurred and the temperature was from 400 °C to the end point of the experiment. The weight loss of the sample during the whole pyrolysis process of S. plumbizincicola was 73.9%. Similar to pyrolysis, the combustion process of the sample can also be divided into three stages. The first step was from room temperature to 185 °C, with about 6.17% biomass weight of S. plumbizincicola lost. The second step was from 185 °C to 400 °C, the fast decomposition stage and similar to the pyrolysis process. About 50.4% of weight of S. plumbizincicola was lost during this stage. Before 400 °C, the pyrolysis and combustion processes had similar DTG curves, indicating that the presence of oxygen did not accelerate the weight loss of the sample at low temperature. At the third step combustion of fixed carbon occurred from 400 to 697 °C. It was observed that the weight loss during combustion was even greater than that during pyrolysis during this stage so that oxidation of inorganic constituents of the sample might have occurred during combustion. The total weight loss of S. plumbizincicola during the combustion process was 89.4%.

Both pyrolysis and combustion of *S. plumbizincicola* were divided into three steps. The weight loss performance of *S. plumbizincicola* was similar in both pyrolysis and combustion conditions at low temperatures, indicating that the presence of oxygen did not accelerate the weight loss of the sample at low temperatures. It was observed that the weight loss during combustion was even greater than that during pyrolysis in the third step, which indicates that oxidation of inorganic ingredients of the sample might occur during combustion. The TG curve of combustion of *S. plumbizincicola* was similar to that of other energy crops, wood or municipal solid wastes [18–21] and appropriate biomass characteristics, low input demand and positive environmental impact. *S. plumbizincicola* is thus a potential renewable energy source and a substitute for the declining supply of fossil fuel resources.

Step	Reagent	Condition
Water soluble Acid soluble Easily reducible Moderately reducible Residual	$ \begin{array}{l} \text{De-ionised water (DW)} \\ 0.5 \ \text{M CH}_3\text{COOH} + 0.1 \ \text{M Ca}(\text{NO}_3)_2 \\ 0.175 \ \text{M (NH}_4)_2\text{C}_2\text{O}_4 + 0.1 \ \text{M H}_2\text{C}_2\text{O}_4 \\ 0.1 \ \text{M Na}_2 \ \text{EDTA} + 0.3 \ \text{M NH}_2\text{OH} \cdot \text{HCl} \\ 10 \ \text{mL HCl} \ 36\% + 5 \ \text{mL HNO}_3 \ 69\% + 2.5 \ \text{mL HF} \ 40\% + 2.5 \ \text{mL DW} \end{array} $	20 °C, 3 h, pH 7, continuous agitation 20 °C, 3 h, pH 5, continuous agitation 95 °C, 3 h, variable agitation, without light 95 °C, 24 h, variable agitation 150 °C, 48–72 h, continuous agitation



Fig. 4. TG/DTG of S. plumbizincicola.

3.2. Effect of temperature on plant heavy metal behaviour

Temperature has a significant impact on the HM volatilization process. The higher the temperature the higher the HM vaporization rate, although the vaporization rate is not linearly proportional to the incineration temperature [22,23]. The recovery of heavy metals is depicted in Fig. 5. The most volatile metal during S. plumbizincicola biomass combustion was Cd. Almost 80.0% of Cd was present in the fly ash and only less than 0.01% occurred in the flow gas. Cd vaporized at temperatures above 380 °C and significant Cd species condensation occurred at temperatures lower than 380 °C and captured by the fly ash [24,25]. At temperatures of 350–650 °C the major portion of Pb (>95%) and Zn (>90%) remained in the bottom ash. Only a minority of lead (almost 3%) and about 10% of Zn were found in the fly ash and were not detectable in the flow gas. The recoveries of Pb and Zn decreased with increasing temperature when T > 650 °C. Therefore, it can be concluded that Pb and Zn were largely volatilized at reactor temperatures above 650 °C and condensation occurred at temperatures below 650 °C. Thus, most of the Pb and Zn were found in the fly ash when the temperature was above 650 °C. Cd and Pb are considered to be more harmful than Zn and the less volatile metals (Zn and Pb) are retained in the bottom ash under low temperatures (<650 °C). Cadmium is more volatile and is concentrated in the fly ash (>80%). The higher the temperature, the higher the HM vaporization rate and more of the metals concentrate in the fly ash, which generally follows the volatilization behaviour of HMs during incineration. HMs initially vaporize in the flame and the resultant metallic vapours then undergo homogeneous nucleation



Fig. 5. Impact of temperature on transport of recovery of HMs during incineration of *S. plumbizincicola* (FA represents fly ash, and BA represents bottom ash).

to form an ultrafine aerosol [26,27]. In the post-incineration region the flue gas cools rapidly and the condensed aerosol of HMs and their oxides increases continuously by heterogeneous coagulation in the fly ash so that less of the HM was found in the flow gas [25].

HM volatility was sensitive to chlorine and sulphur contents, S/Cl ratio, and the content of alkali metals [28,29]. Fig. 6 shows that heavy metal volatile compounds occurred preferentially with Cl as CaCl₂ and KCl because the ratio of (S + Cl)/(alkali metals) was about 0.02 (w/w) in our experiments, i.e. the alkali metals were in strong abundance and they tended to react with Cl to form CaCl₂ and KCl, suggesting a stronger influence on decreasing the volatility of the HMs. Sulphur, iron, aluminium, and silicates have been reported to be important compounds in the vapour of heavy metals [26,30]. Fig. 6b shows that most of the S. Fe, Al, and SiO₂were found as SO₂, $Fe_2(SO_4)_3$, Fe_2O_3 , FeO, $Ca_3Al_2O_6$, K₂SiO₃, and SiO₂ during the combustion process instead of reacting with HMs. Therefore, the partitioning of HMs during the combustion process varies significantly with the element type. Fig. 6a shows the equilibrium distributions of different HMs in the temperature range of 350–1950 °C for a typical air excess ratio a = 1.2. Zn was found as Zn, ZnO, Zn₂SiO₄, ZnSiO₃, and ZnCO₃. When the temperature was >650 °C, Zn, Zn₂SiO₄, ZnSiO₃, and ZnCO₃ decreased and ZnO increased with increasing temperature. Cd was found mainly as Cd and CdO. At low temperatures (<750 °C) CdSiO₃ was found and decreased with increasing temperature. Pb was the major species at low temperatures (<750 °C); at higher temperatures PbO was the dominant species. Because of the low concentration of Cl (1135 \pm 15 mg/kg) in *S. plumbizincicola*, easily volatilized CdCl₂ and PbCl₂ were not found. Thus, most of the Zn, Cd and Pb were present as pure metals and their oxides. The powdered XRD patterns of fly ash and bottom ash are



Fig. 6. Equilibrium distribution of HMs versus temperature of *S. plumbizincicola* simulated by Aspen.

shown in Fig. 7. In combustion conditions crystalline phases of Zn in the bottom ash at 850 °C were found as ZnO and Zn(OH)₂, and Zn, Zn₂Cu(AsO₄)₂, and Zn₂Cu(AsO₄)₂ were found in the fly ash. Crystalline phases of Cd in the bottom ash were found as CdO and CaO_{0.67}Cd_{0.33}CO₃ in bottom ash and Cd in the fly ash. At 650 °C alumino-ZnO and ferric oxide-Pb were found but crystalline phases of Cd were not found. The results of the sequential chemical extraction (Fig. 8) show that Cd, Zn, and Pb had weak mobility and were mainly in the 'acid soluble', 'moderately reducible' and 'residual', fractions so that the metals were associated with carbonates, silicates, alumino-silicates, crystalline pure metals or as crystalline oxides [30].

The mineral matter content of waste affects the heavy metal partitioning through the formation of binary or ternary oxides that can greatly decrease the volatilization of metals [31,32]. The presence of SiO₂ and Al₂O₃ can lead to the formation of stable HM salts (silicates and meta-aluminates) and function as sorbents [5]. However, in the present study the alkali present tended to react with SiO₂ and Al₂O₃ to form alkali salts instead of HM salts.

3.3. Impact of air flow rate on behaviour of heavy metals

The air flow rate is an important parameter controlling the combustion process [33]. The conventional mass burn systems require 20-100%excess air over the stoichiometric value [34], resulting in an oxidizing atmosphere in a typical incinerator. Nevertheless, reducing conditions may exist around and inside combusting particles in the combustion zone even if the air supply is above the theoretical value. The influence of the total air flow rate (characterised by the air excess ratio) was studied at 850 °C and both reducing and oxidizing conditions were considered by varying air flow rate between 0.5 and 1.2 L/min. The results for Zn, Cd, and Pb are displayed in Fig. 9. For Cd and Pb the recovery rates from fly ash are higher than from bottom ash. The recoveries of Zn, Pb, and Cd fluctuated with increasing air flow rate. More Pb and Cd were found in the bottom ash under the reduced conditions (air flow rate <0.75 L/min) than the oxidized conditions, while more Zn was found in the bottom ash during the oxidized conditions.

Fig. 10 shows the equilibrium distributions of different HMs in an air excess ratio range of 0.2–2 for a typical temperature of 850 °C. Zn is alternatively found as Zn, ZnO, and ZnS when a < 0.6, and only ZnO was found when a > 0.6. Cd and CdS were found in reducing conditions (a < 1), while CdO and Cd were found when a > 0.2. Pb and PbS were the dominant species when a < 1 and the mass of PbO increased with increasing air excess ratio. Concentrations of Cl in *S. plumbizincicola* were low, and PbCl₂ and ZnCl₂ were formed when a < 0.4 and a < 1, respectively. However, most Zn, Cd, and Pb existed as Zn, ZnO, ZnS, Cd, CdS, Pb, and PbS in reducing conditions (Fig. 4). From the point of view of environmental protection, combustion would be better as a potential choice for thermal treatment of hyper-accumulators.

In pyrolysis conditions crystalline phases of Cd, Zn, and Pb in the bottom ash were found as $Ca_{0.75}Cd_{0.25}O$, $Pb_2O_{3.333}$, and ZnS (Fig. 7c). In the fly ash crystalline phases of Zn were found as ZnO, ZnS, and organic-Zn, and phases of Cd and Pb were found to form complex compounds with other metals (Cu, Al, and Ag) (Fig. 7e).

The sequential extractions of Cd and Pb showed a weak mobility in bottom ash (Fig. 11). In contrast, Zn was mainly in easily leachable phases, indicating that Zn may be present as the carbonate or as free metal. Moreover, much of the Pb and Cd were mainly in the 'moderately reducible' and 'residual' fractions. Also, according to the results of the equilibrium distributions (Fig. 6) and XRD (Fig. 7c and Fig. 7e), the phases of Cd, Zn, and Pb could be pure metals, crystalline oxides,

Fig. 7. Powdered XRD patterns of fly ash and bottom ash. X-ray diffraction traces for $2\theta = 13-90^{\circ}$ Cu K α radiation. Vertical bars in various colours refer to the 2 θ positions of the X-ray reflections for the 8 crystalline phases (A: bottom ash of combustion at 650 °C, B: bottom ash of combustion at 850 °C, C: bottom ash of pyrolysis at 850 °C, D: fly ash of combustion at 850 °C).





Fig. 8. Results of sequential chemical extraction for Cd, Zn, and Pb versus temperature.



Fig. 9. The impact of air flow rate on transport of recovery of HMs during incineration of *S. plumbizincicola*.



Fig. 10. Equilibrium distribution of HMs versus air excess ratio of *S. plumbizincicola* simulated by Aspen.

sulphides or more complex compounds. Cl, Al₂O₃, and SiO₂ showed little effect on the vapour of HMs during the reductive conditions because they were present mostly as alkali salts. At higher temperatures (>850 °C) both the oxidizing atmosphere and reducing conditions favour the transfer of HMs such as Cd, Pb, and Zn to the fly ash phase as is observed in municipal solid waste incineration [35]. The recoveries of Zn, Pb, and Cd fluctuated with increasing air flow rate. More Pb and Cd were found in the bottom ash under reducing conditions (air flow rate < 0.75 L/min) than oxidizing conditions.

Taken together with our previous in vitro data, the results indicate that more Pb and Cd were found in the bottom ash under the reducing conditions (air flow rate < 0.75 L/min) than the oxidizing conditions because the Pb and Cd form heavy metal complex compounds such as Ca_{0.75}Cd_{0.25}O, Pb₂O_{3.333} or complex compounds with other metals (Cu, Al, and Ag) which were in the 'moderately reducible fraction' and 'residual fraction' in the sequential extractions of Cd and Pb. However more Zn was found in the bottom ash during the oxidizing conditions because Zn should be in the Zn(g) form in reducing conditions above 850 °C. Further reactions that have to be considered are the subsequent homogeneous reactions in the gaseous phase. The oxidation of volatile zinc by carbon dioxide to solid zinc oxide and carbon monoxide (reaction 1) and especially the homogeneous oxidation of gaseous zinc by steam to solid zinc oxide and hydrogen (reaction 2) proceed at temperatures above 750 °C and are described for pyrometallurgic processes [36,37].

 $Zn(g) + CO_2 = ZnO(s) + CO(g)$



Fig. 11. Sequential chemical extraction for Cd, Zn, and Pb versus oxygen content.

$$Zn(g) + H_2O = ZnO(s) + H_2(g)$$
⁽²⁾

Moreover, ZnO can react with H₂S to form zinc sulphide (reaction 3).

$$ZnO(s) + H_2S(g) = ZnS(g) + H_2O(g)$$
(3)

Therefore, the explanation for the lower recovery of Zn in bottom ash in reducing conditions is the higher volatility of Zn in the flow gas in ZnO and ZnS forms which are captured in the fly ash (Fig. 7e).

4. Conclusions

Experimental investigation and thermodynamic equilibrium calculations were carried out to identify the transformation and the possible reactions of HMs during the thermal disposal of a Zn and Cd hyperaccumulator - S. plumbizincicola biomass.

It is optimal to maintain the temperature above 700 °C with excess air supply in the thermal disposal of *S. plumbizincicola*. Most Cl, S, Fe, Al, and SiO₂ were found as CaCl₂, KCl, SO₂, Fe₂(SO₄)₃, Fe₂O₃, FeO, Ca₃Al₂O₆, K₂SiO₃, and SiO₂ during the combustion process instead of reacting with HMs.

The likeliest chemical forms of Pb in combustion conditions are the pure metal and its oxide in both fly ash and bottom ash. For Cd and Zn, possible components are the pure metals, their oxides and carbonates, and silicate compounds may be found under low temperature conditions. Under reducing conditions, Pb and Cd form heavy metal complex compounds such as $Ca_{0.75}Cd_{0.25}O$, $Pb_2O_{3.333}$ or complex compounds with other metals (Cu, Al, and Ag) while Zn can be pure metal, crystalline oxide, sulphide or complex compounds with other metals.

Most of the original mass of *S. plumbizincicola* was reduced. Fly ash and/or bottom ash fractions were given high enrichment (>99%) in Cd, Pb, and Zn after the thermal disposal. Thermal disposal of *S. plumbizincicola* might allow the achievement of a sustainable and environmentally safe production of energy from HM-polluted land.

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